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�54 Cloth prepreg and process for producing it.

�57 A prepreg suitable for preparing honeycomb sandwich panels, by which the formation of pores in interlayer zones of a cured composite can be reduced, comprises a resin composition including an epoxy resin, a curing agent and a solid rubber, and a woven fabric made of reinforcing fibers, the meshes of the woven fabric being crushed such that said prepreg has a cover factor K_p of 97 - 99.9%.

EP 0 559 437 A1

BACKGROUND OF THE INVENTION

The present invention relates to a cloth prepreg and process for producing it. More particularly, the present invention relates to a cloth prepreg which gives a fiber-reinforced plastic (hereinafter also referred to as "FRP") having high toughness and high modulus of elasticity as well as high thermal resistance, low water absorption and good solvent resistance, and which hardly forms pores in the FRP plate prepared by the so called honeycomb co-curing using the prepreg, and to a prepreg which gives an FRP having a good burn-through property.

Epoxy resins are widely used in various industrial fields as molded articles, laminated articles, adhesives, sealants and the like exploiting their excellent mechanical properties, high chemical resistances and the like. Fiber-reinforced composite materials which have reinforcing fibers and matrix resins as indispensable constituents are used as structural materials of airplanes, automobiles and the like, and epoxy resins are widely used therein. Particularly, carbon fiber-reinforced plastics (CFRP) are conventionally used as structural materials of airplanes. To reduce the weight of the airplanes, honeycomb sandwich panel structure is often employed. The honeycomb sandwich panel structure is prepared by laying up prepregs on both sides of a honeycomb coro made of aramide paper or the like (in some cases, via adhesive films), and the curing of the prepregs and the adhesion of prepregs to the honeycomb core are simultaneously carried out (this curing is called honeycomb co-curing). Thus, good co-curing properties are demanded for the prepregs.

It is also demanded that pores be not formed in the FRPs of the honeycomb sandwich panel. Since no pressure is applied to the regions of the prepregs on and under the inner space of the hexagonal cells in the honeycomb core, pores and likely to be formed in the interlayer zones and within one prepreg layer. If a molded plate having such pores are used to constitute a spoiler of an airplane, water is accumulated in the pores and when the airplanes flies at high altitude, the water is frozen to crack the skin (i.e., FRP of the sandwich panel). By repeating this, water comes to enter the honeycomb core and the physical properties of the panel is degraded, so that safe operation of the airplane is jeopardized. In other words, if the porosity of the FRPs are high, the reliability as a fiber-reinforced composite material is degraded.

There is the following prior art concerning the prepreg employing carbon fibers as reinforcing fibers and concerning matrix resins, which are designed to be used for the honeycomb co-curing.

Japanese Patent Publication (Kokoku) Nos. 63-30925 and 1-29814 disclose the following epoxy resin composition by which good direct adhesion between the prepregs and the honeycomb core and good composite properties of the cured plate as a surface material, especially, high interlayer shearing strength (ILSS) are attained. That is, as the epoxy resin, three types of epoxy resins, that is, bisphenol A type, novolak type and glycidylamine type are selected. The resin composition further comprises a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and a glycidylamine type epoxy resin, as well as nitrile rubber and dicyandiamide as a curing agent. The content of each component is made within a prescribed range by which the above-mentioned properties are stated to be attained. Japanese Patent Publication (Kokoku) No. 62-28167 discloses as a matrix resin suited for hybrid reinforcing fibers including carbon fibers and aromatic polyamide fibers, a composite comprising an epoxy resin, a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and an epoxy resin, and dicyandiamide, as well as liquid or semi-solid polyamide having amino group at its end. Japanese Laid-open Patent Application (Kokai) Nos. 58-82755, 58-83022 and 58-83031 disclose that by employing a composition containing a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and an epoxy resin, and both dicyandiamide and diaminodiphenylsulfone as curing agents, direct adhesion between the prepregs and the honeycomb core is promoted, especially at a high temperature.

Japanese Laid-open Patent Application (Kokai) Nos. 57-21427 and 57-21450 disclose that a prepreg prepared by impregnating into fibers a resin solution obtained by dissolving a composition containing an epoxy resin, a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and an epoxy resin, nitrile rubber and a curing agent represented by dicyandiamide, in acetone-methyl Cellosolve mixed solvent or the like gives excellent adhesion strenght, high impact strength and high bending strength to the honeycomb sandwich panel.

Japanese Laid-open Patent Application (Kokai) No. 57-49646 discloses that a prepreg employing a resin composition comprising an epoxy resin, nitrile rubber and a high molecular epoxy resin having a molecular weight of not less than 10,000 exhibits good direct adhesion to the honeycomb core, so that it gives high adhesion strength and high bending strength to the honeycomb sandwich panel. In the examples thereof, dicyandiamide is used as a curing agent and prepregs are prepared by dissolving the composition in acetone-methyl Cellosolve mixed solvent or the like.

Japanese Laid-open Patent Application (Kokai) No. 58-84825 discloses a prepreg in which an epoxy resin composition containing a bisphenol A type epoxy resin, an urethane-modified epoxy resin, an epoxy resin hav-

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ing N,N-diglycidylamino group, a brominated bisphenol A type epoxy resin and dicyandiamide is impregnated. It is described that the honeycomb sandwich panel employing this prepreg has excellent high heel resistance and high bending strength.

However, the above-mentioned prior art does not aim at reducing the porosity in the interlayer zones.

Further, if diaminodiphenyl sulfone alone is used as a curing agent which gives high thermal resistance, pores are much more easily formed in the interlayer zones than in cases where dicyandiamide is used as a curing agent, and this problem is very difficult to solve.

SUMMARY OF THE INVENTION

Accordingly, the present invention seeks to provide a prepreg which hardly forms pores in the cured FRP plates even when diaminodiphenylsulfone is used as a curing agent, which gives an FRP having high toughness and high modulus of elasticity as well as high thermal resistance, low water absorption and good solvent resistance, which has good tackiness and drapability and which gives an FRP having a good burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials.

The present invention provides a cloth prepreg comprising a resin composition including an epoxy resin, a curing agent and a rubber (preferably solid), and a woven fabric made of reinforcing fibers, the meshes of said woven fabric being such that said prepreg has a cover factor K_p of 97 - 99.9%. The desired cover factor may be achieved by crushing of the meshes.

The present invention also provides a process of producing the cloth prepreg, comprising impregnating the resin composition containing a solid acrylonitrile-butadiene rubber having a functional group and a weakly cross-linked structure into the woven fabric in two steps, wherein in the first impregnation step, the resin composition is impregnated so as to attain a resin content W_R of 10 - 30%.

The present invention further provides a process of producing the cloth prepreg, comprising the step of impregnating a resin composition containing an epoxy resin, a curing agent and a solid acrylonitrile-butadiene rubber having a functional group and not having a cross-linked structure into a woven fabric having warps and woofs made of multifilament carbon fibers, the widths W (mm) and finenesses D (denier) of said warps and woofs satisfying the equation of:

$$W = k \cdot (D/\rho)^{5/9}$$

(wherein k represents $3.5 \times 10^{-2} - 10.0 \times 10^{-2}$ (mm·$D^{-5/9}$) and ρ represents specific gravity of said carbon fibers), said woven fabric having a cover factor K_c of 90.0 - 99.8%.

The cloth prepreg of the present invention does not substantially form pores in the cured FRP plates when subjected to honeycomb co-curing, and gives FRP having high toughness, high modulus of elasticity, as well as high thermal resistance, low water absorption and high solvent resistance. The prepreg also has good tackiness and drapability. Further, the cloth prepreg gives an FRP having a good burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Example 1 after polishing;

Fig. 2 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Comparative Example 1 after polishing;

Fig. 3 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Example 3 after polishing; and

Fig. 4 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Comparative Example 7 after polishing.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A component constituting the epoxy resin composition used in the present invention is an epoxy resin. Epoxy resin means a resin having not less than two epoxy groups on average per one molecule.

Preferred examples of the epoxy resins which are derived from amines include tetraglycidyl diaminodiphenylmethane, triglycidyl-p-aminophenol, triglycidyl-m-aminophenol and triglycidyl aminocresol. Among these, tetraglycidyl diaminodiphenylmethane is especially preferred as a resin for composite material for a structural material of airplanes because it has excellent thermal resistance.

Preferred examples of the epoxy resins derived from phenols include bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol novolak type epoxy resins, cresol novolak

type epoxy resins and resorcinol type epoxy resins. Since liquid bisphenol A type epoxy resins and bisphenol F type epoxy resins have low viscosities, they are suited for blending other epoxy resins and additives.

Preferred examples of the epoxy resins derived from compounds having carbon-carbon double bonds include alicyclic epoxy resins. Brominated epoxy resins obtained by brominating these alicyclic epoxy resins are also preferred since the water absorption of the resin is decreased and environment resistance is promoted.

The epoxy resin may be a mixture of two or more epoxy resins and may contain a mono-epoxy compound. The combination of a glycidylamine type epoxy resin and a glycidyl ether type epoxy resin is preferred because it simultaneously satisfies good thermal resistance, water resistance and processability.

In view of the balance of heat resistance, water resistance and processability, the combination of the following epoxy resins in the amounts shown is especially preferred.

Bisphenol A type epoxy resin	10 - 60 wt%
Brominated bisphenol A type epoxy resin	0 - 30 wt%
Tetraglycidyldiaminodiphenyl methane	10 - 40 wt%
Bisphenol F type epoxy resin	5 - 40 wt%

Another component constituting the epoxy resin composition used in the present invention is a curing agent. Any compound having active groups which can react with epoxy group may be employed as the curing agent. Compounds having amino groups, acid anhydride groups, azide groups and hydroxy groups may preferably be employed.

For example, dicyandiamide, various isomers of diaminodiphenyl sulfone, aminobenzoates, various acid anhydrides, phenol novolak resins and cresol novolak resins may be employed. Dicyandiamide is preferred because it gives long shelf-life of prepreg. If an aromatic diamine is used as a curing agent, cured epoxy resin having good thermal resistance can be obtained. In particular, various isomers of diaminodiphenyl sulfone are best preferred in the present invention since they give cured resins with good thermal resistance. Diaminodiphenyl sulfone may preferably be used in an amount such that the amount of its active hydrogen is 0.7 - 1.2 equivalent with respect to the amount of the epoxy groups of the epoxy resin. As the aminobenzoates, trimethyleneglycol-di-p-aminobenzoate and neopentylglycol-di-p-aminobenzoate may preferably be used. Although the resins obtained by using those curing agents have lower thermal resistances than those obtained by using diaminodiphenylsulfone, since they excel in tensile strength and toughness, they may be selected depending on the intended use. If an acid anhydride represented by phthalic anhydride is used as a curing agent, cured resin with good thermal resistance is obtained, and an epoxy resin composition having low viscosity and so having excellent processability can be obtained. A phenol novolak resin or a cresol novolak resin may also preferably be used as a curing agent since ether bonds having good hydrolysis resistance are introduced into the molecular chains, so that the water resistance of the cured resin is promoted.

Further, various curing catalysts may also be employed together with the above-mentioned curing agents. A representative example of the curing catalysts is monoethylamine complex of trifluoroboron. Cyanate resins (triazine resins) may also be employed together with the epoxy resin. In this case, a curing reaction takes place between the cyanate and the epoxy groups, so that a cured resin with low water absorption can be obtained.

The epoxy resin composition used in the present invention further comprises a solid rubber. Solid rubber herein means a rubber which does not have flowability at room temperature. The material of the rubber may be any elastomer.

By adding the solid rubber to the epoxy resin, a resin having high viscosity and high thixotropic property is obtained. During the fabrication, the matrix resin is in a quiescent state to which shearing force is not applied. The high thixotropic property means that the viscosity of the matrix resin is high in such a quiescent state. By virtue of this property of the resin, the formation of pores during the fabrication can be reduced. The rubber especially suited for giving high thixotropic property to the epoxy resin is solid acrylonitrile-butadiene rubber (acrylonitrile-butadiene rubber is hereinafter also referred to as "NBR") having a functional group and a weakly cross-linked structure. The term "weakly cross-linked" means that the rubber is cross-linked to such a degree that the rubber is swollen by a solvent but not dissolved in the solvent.

It is preferred that the solid rubber be three-dimensionally swollen and microdispersed in the epoxy resin so that it partially forms network, and that the solid rubber be not uniformly dissolved. Especially, the above-mentioned rubber having the weakly cross-linked structure is preferred since it always "phase-separated" from the non-cured state to the cured state, and is not uniformly dissolved at any time point. Although the degree of microdispersion of the solid rubber varies depending on the method of mixing and on the composition of the epoxy resin, the width of the rubber phase may preferably be 0.1 - 10 μm. If the dispersed phase is too

small, the viscosity of the resin is unnecessarily decreased, and if the dispersed phase is too large, it hinders the impregnation to the reinforcing woven fabric so that it may be difficult to obtain a prepreg having uniform composition. In view of this, the width of the rubber phase may more preferably be 0.5 - 5 μm.

It should be noted that an epoxy resin composition having high thixotropic property may also be obtained by using a solid rubber which does not have a cross-linked structure, if an appropriate amount is used. This is also a preferred mode of the present invention.

Further, the solid rubber which does not have a cross-linked structure has relatively low viscosity, so that if a woven fabric of carbon fibers which satisfy the below-described specific equation and which have the below-described specific cover factor K_c is used as a reinforcing fabric, the object of the present invention may easily be attained. This is also a preferred mode of the present invention.

By the addition of the solid rubber, adhesiveness and flexibility of the resin composition are also promoted, so that the tackiness and drapability of the prepreg, which are important characteristics for prepregs, are promoted.

The solid rubber used in the present invention may preferably have a functional group which reacts with the epoxy resin or the curing agent. By this, the solvent resistance and mechanical properties of the cured resin are promoted. Especially preferred functional group is carboxylic group.

It is also preferred to add polyether sulfones to the epoxy resin composition, since the viscosity of the resin composition as well as the tackiness and drapability of the prepreg may easily be controlled. In view of the compatibility with the epoxy resin, polyether sulfones having hydroxyl group at the terminals are preferred.

The content of the solid rubber in 100 parts by weight of the matrix resin composition may preferably be 3 - 12 parts by weight, more preferably 5 - 10 parts by weight, in view of preventing the too much decrease in the thermal resistance of the composite, and preventing the generation of pores due to the low viscosity of the resin. On the other hand, the content of the polyether sulfone in 100 parts by weight of the matrix resin composition may preferably be not more than 5 parts by weight, more preferably 1 - 4 parts by weight, in view of preventing prominent decrease in the tackiness and drapability of the prepreg.

In cases where the resin composition contains a solid rubber having a weakly cross-linked structure, the resin composition may preferably have a complex coefficient of viscosity $\eta_{0.02}$ measured at 80°C under a vibration frequency of 0.02 Hz of not less than 5000 poise, more preferably not less than 20,000 poise, in view of keeping high viscosity in the quiescent state so as to reduce the porosity during the fabrication of the prepreg.

The complex coefficient of viscosity may be determined as follows using MR-3 Soliquid Meter commercially available from Rheology Co., Ltd.

That is, a plate-plate type (parallel plate type) system employing plates having a diameter of 1.798 cm and a gap between the plates of 0.5 mm is used. The measuring atmosphere is kept at 80°C. A sample is filled between the plates, and one of the plates is vibrated with a prescribed frequency to a amplitude of 1°. From the torque and phase difference generated by the vibration, the complex coefficient of viscosity is determined.

By measuring the complex coefficient of viscosity under the frequency from 0.02 - 2 Hz, the frequency dependence of the complex coefficient of viscosity can be determined.

Especially in cases where the resin composition contains the solid rubber having a weakly cross-linked structure, it is preferred that the complex coefficient of viscosity η_2 of the resin composition measured at a frequency of 2 Hz and a complex coefficient of viscosity $\eta_{0.02}$ measured at 0.02 Hz satisfy the equation of

$$\log\eta_{0.02} - \log\eta_2 \geqq 0.5$$

in view of lowering the viscosity in the state that shearing force is applied, thereby assuring the easy coating of the resin film which tends to be difficult when the resin has a high viscosity.

Especially in cases where the resin composition contains the solid rubber which does not have a cross-linked structure, in view of promoting impregnation property of the prepreg while keeping a good film coating property and while reducing the porosity, the resin composition may preferably have a complex coefficient of viscosity $\eta_{0.5}$ determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min (hereinafter referred to as "complex coefficient of viscosity $\eta_{0.5}$ at 80°C" for short) of 100 - 1500 poise, and have a minimum complex coefficient of viscosity η_{min} determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 50 - 300 poise.

Especially in cases where the resin composition contains a solid rubber not having a cross-linked structure, it is preferred to employ a woven fabric made of carbon fibers which satisfy the equation of $W = k \cdot (D/\rho)^{5/9}$ and having a cover factor K_c of 90.0 - 99.8% as described below in detail, since especially advantageous effects are obtained.

The reinforcing fibers constituting the woven fabric may be any fiber which is used as a advanced composite material having good thermal resistance and tensile strenght. Examples of the fibers include carbon fibers, graphite fibers, aramide fibers, silicon carbide fibers, alumina fibers, boron fibers, tungsten-carbide fib-

ers and glass fibers. Among these, carbon fibers and graphite fibers are especially preferred since they have high specific strength and high specific elastic modulus, and they largely contribute to the light weight of the prepreg.

Although any type of carbon fibers and graphite fibers may be employed depending on the intended use, high strength, high elongation carbon fibers having a tensile strength of not less than 350 kgf/mm^2 and a tensile elongation of not less than 1.5% are best preferred.

The reinforcing woven fabric made of the reinforcing fibers may be a conventional two-dimensional woven fabric. Biaxially woven fabrics having a fabric tissue in which warps and woofs cross at right angles, such as plane weaving, twill or satin are preferred.

Especially in cases where the resin composition contains a solid rubber which does not have a cross-linked structure, in view of reducing the porosity, it is preferred to use a reinforcing woven fabric which has warps and woofs made of multifilament carbon fibers, the widths W (mm) and finenesses D (denier) of the warps and woofs satisfying the equation of:

$$W = k \cdot (D/\rho)^{5/9}$$

(wherein k represents 3.5×10^{-2} - 10.0×10^{-2} (mm·D$^{-5/9}$) and ρ represents specific gravity of the carbon fibers), and which has a cover factor K_c of 90.0 - 99.8%.

The cover factor K_c is the cover factor of the woven fabric, which relates to the size of the mesh of the woven fabric. The cover factor K_c may be determined as follows. That is, a region having an area S_1 is defined on a woven fabric. C_f which is defined by the equation of:

$$C_f = [(S_1 - S_2)/S_1] \times 100$$

is determined for optional 10 regions. The arithmetic average is defined as cover factor K_c. The larger the cover factor K_c, the more progressed the opening of the filaments, the enlargement of the width of the filaments and the flattening of the filaments, and the smaller the mesh of the woven fabric.

In order to avoid the formation of a region in the skin of the composite, in which carbon fibers do not exist, in which resin is too much, or in which voids are contained, it seems that the cover factor K_c is preferably 100%, that is, the meshes are completely crushed. However, in such a woven fabric, the filaments are too much restrained each other and the freedom in the movement of the filaments are too small, so that the prepreg has poor drapability and wrinkles are likely to be formed. Thus, it is preferred to provide a very small clearance among the filaments so as to assure freedom in deforming. In view of the balance between the degree of opening, width-enlargement and flattening of the filaments and the drapability, the upper limit of the cover factor is preferably 99.8%.

The concrete method for measuring the cover factor K_c of the woven fabric may be as follows:

First, using a stereoscopic microscope, e.g., stereomicroscope SMZ-10-1 commercially available from Nikon, a photograph of the surface of the fabric is taken while illuminating the back side of the fabric. Thus, in the photograph, the transmitted light pattern is shown, wherein the filaments are black and meshes are white. The intensity of the illumination light is so controlled that halation does not occur. In the examples hereinbelow described, the light from the double arm fiber commercially available from Nikon is used after reflected by an acryl plate. The magnification of the photograph is set to not less than 10 magnification so that 2 - 20 warps and woofs are contained, respectively. The obtained photograph is then photographed using a CDC (charge coupled device) camera and the image is then converted to digital data indicating white and black. The data are stored in a memory and then processed with an image processing apparatus to calculate the C_f according to the above-mentioned equation from the total area S_1 and the total area S_2 of the white portions. The above-mentioned procedure is repeated 10 times for different portions of the same fabric, and the arithmetic average is defined as cover factor K_c of the fabric. In the Examples later described, Personal Image Analyzing System LA-525 commercially available from Pierce Co., Ltd. was used as the CCD camera and the image processing apparatus. The range of the image-analyzed area was from the left most of portion of the left most warp to the right most portion of the right most woof, and from the upper most portion of the upper most woof to the lower most portion of the lower most woof. Within this range, 2 - 20 warps and woofs are included, respectively. In the digital data, intermediate portions (between white and black) is included between the filaments (black portion) and meshes (white portion). To clearly allocate the intermediate portions to the filament portions or mesh portions, black tapes having a width of 6 mm were stuck on a transparent paper such that the tapes form a lattice. The lattice was normalized to have a cover factor of 75%. That is, the iris diaphragm of the CCD camera was set to 2.8, and the memory value of not more than 128 in the image analyzing system LA-525 was normalized to be filament portion (In this system, the light and shade of the white and black is recorded as memory values of 0 - 255 grades.)

Such a woven fabric can be produced by, for example, as follows:

First, a woven fabric having warps and woofs made of multifilaments of carbon fibers is produced by an ordinary weaving operation.

In view of the ease of weaving operation and of the uniformity of the dispersion of single fibers in a filament after the below-described operation for opening, width-enlarging and flattening operation, the number of single fibers constituting a filament may preferably be 3,000 - 30,000, and the fineness of the filament may preferably be 1,200 - 40,000 denier. The diameter of a single fiber may preferably be 5 - 10 μm. To make the opening, width-enlarging and flattening operation of the fibers easy and uniform, the number of twisting of the filament may preferably be not more than 5 turns/m. Although from the view point of the opening, width-enlarging and flattening operation, filaments which are not twisted at all are preferred, but weaving non-twisted filaments may be somewhat difficult.

In cases where the multifilaments of the carbon fibers are used for preparing the woven fabric, to attain easy and uniform operation for opening, width-enlarging and flattening, it is preferred to make the clearances among the warps and woofs (i.e., the meshes) larger than those of the ordinary fabric. The degree thereof depends on the width of the filaments, but the width of the meshes is preferably at least 1/5 of the width of the warps. When the width of the warps is 1.5 mm, the best width of the meshes is about 0.5 mm.

The fabric tissue may preferably be plain weaving. It is best preferred that the warps and woofs have the same number of carbon fibers per filament and have the same fineness, and that the weaving densities of the warps and woofs be the same.

The weight of the woven fabric per a unit area may optionally be selected. In view of ease and uniformity of the opening, width-enlarging and flattening operation, and in view of the shape-retaining ability and of the cover factor K_c, the weight of the woven fabric may preferably be 120 - 250 g/m², more preferably 140 - 195 g/m². This range of weight is especially preferred when the number of single fibers per filament is 3,000. It should be noted that the weight per a unit area is not changed before and after the opening, width-enlarging and flattening operation of the filaments.

The woven fabric is then subjected to the operation for opening, width-enlarging and flattening the filaments constituting the warps and woofs. This may be carried out by continuously feeding the woven fabric in the direction of warps and treating the woven fabric with water jets from a plurality of nozzles arranged in the direction of the woofs.

For the ease of the operation for opening, width-enlarging and flattening the filaments constituting the warps and woofs, the diameter of the holes in the nozzles may preferably be 0.05 - 0.5 mm, the nozzle pitch may preferably be not more than 1/3 of the pitch of the woofs of the fabric, and the beating force per one water jet may preferably be 0.1 - 3 gf.

By this operation, the warps and woofs may easily attain the widths and finenesses which satisfy the above-described equation of:

$$W = k\cdot(D/\rho)^{5/9}.$$

In the woven fabrics which satisfy this equation, the filaments are very uniformly opened, width-enlarged and flattened, and the bending at the intersections of warps and woofs is very small so that they excel in surface smoothness. It should be noted that "k" in the above-described equation relates to the degree and uniformity of the opening, width-enlarging and flattening of the filaments, and if the "k" is lower than the above-mentioned lower limit, the width-enlarging and flattening are not sufficiently progressed, so that the bending at the intersections of the filaments is large and the irregularity in the surface is also large. On the other hand, if the "k" is more than the above-described upper limit, the degree of opening of the filaments is uneven.

Among the woven fabrics described above, those in which the warps and woofs are made of multifilaments having the same number of single fibers per filament and have the same fineness, of which fabric tissue is plain weaving, whose warps and woofs satisfy the above-described equation of $W = k\cdot(D/\rho)^{5/9}$, whose weaving densities in the directions of the warps and woofs are the same, whose weight is within the range of 120 - 250 g/m², and which has a cover factor K_c within the range of 90 - 99.8% are especially suited for the present invention. If the number of single fibers per multifilament is 3000, the fabric is even more preferred.

In general, woven fabrics, except for those having specific fabric tissues, are highly anistoropic since the warps and woofs extend in the directions which are at right angles. However, if the numbers of fibers per multifilament in the warps and woofs, as well as the finenesses of the warps and woofs are identical, the characteristics in the directions at right angles are the same. Therefore, by laying-up the fabrics shifting a prescribed angle, e.g., 45°, pseudo-isotropic characteristics can easily be attained. Further, from the view point of manufacturing process, if the number of single fibers per filament and the finenesses of the warps and woofs are identical, and if the weaving densities are identical in the warp and woof directions, the size of a mesh is identical in the warp and woof directions. Therefore, by opening the multifilaments to the same degree in both the directions, the width-enlarging and flattening of the filaments can easily be attained.

Further, if the fabric tissue is plain weaving, a thin and stable woven fabric in which the deformation of the meshes is small, may be obtained.

Further, if the number of single fibers per filament and the finenesses of the warps and woofs are identical,

if the weaving densities are identical in the warp and woof directions, and if the weight is 120 - 250 g/m², the cover factor K_c is not too small, the bending of the multifilaments at the intersections is smaller, so that the breakage by the concentration of stress can surely be avoided, and the irregularity in the surface is small, thus it is preferred. From the view point of manufacturing process, in the fabric such a weight per a unit area, the restraint by the filaments each other is small in spite of the fact that the fabric tissue is plain weaving, and the size of the mesh is small, so that the opening, width-enlarging and flattening of the filaments can be easily attained with water jets. The weight of the fabric may more preferably be 140 - 195 g/m².

As the resin composition to be impregnated to such a woven fabric that satisfies the above-described equation of $W = k \cdot (D/\rho)^{5/9}$ and has a cover factor K_c of 90 - 99.8%, since resin compositions having relatively low viscosities are preferred to reduce the porosity, a resin composition containing an epoxy resin, a curing agent and a solid NBR which has a functional group and does not have a cross-linked structure is preferred.

It is more preferred that the resin composition just mentioned above have a complex coefficient of viscosity $\eta_{0.5}$ determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 100 - 1500 poise, and has a minimum complex coefficient of viscosity η_{min} determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 50 - 300 poise.

For the purpose of controlling the viscosity of the resin, or improving physical properties of the composite, such as compression strenght and toughness, the cloth prepreg of the present invention may contain particles of calcium carbonate, talc, mica, silica, carbon black, silicon carbide, alumina hydrate or the like. The content of such particles is not restricted, but must not adversely affect the advantageous effects of the present invention. The content of the particles may usually be 0.1 to 3.0% based on the weight of the epoxy resin composition.

The cover factor K_p of the cloth prepreg of the present invention is 97 - 99.9 %. It should be noted that the cover factor K_p is not the above-described cover factor K_c of the woven fabric, but is the cover factor of the cloth prepreg after the resin composition is impregnated into the woven fabrics.

If the cover factor K_p is less than 97%, the degree of crushing of the meshes which are clearances formed among the warps and woofs of the reinforcing woven fabric is insufficient, so that pores are likely to be formed in the honeycomb fabricated plate, and the burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials, is not promoted. On the other hand, if the cover factor K_p is more than 99.9%, the drapability which is an important characteristic of a prepreg, is largely decreased.

In contrast, if the cover factor K_p is within the range of 97 - 99.9%, the porosity of the honeycomb fabricated panel is largely decreased while keeping the good drapability intrinsic to the cloth prepreg.

Further, in the cured plate obtained by curing the above-described cloth prepreg, the reinforcing fibers are uniformly distributed and the cover factor is large, so that cured plate excels in the burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials.

The cover factor K_p is determined by the same method as the above-described method for determining the cover factor K_c, except that cloth prepreg is subjected to the measurement in place of the woven fabric.

The prepreg of the present invention may be prepared, in principle, by a conventional method for producing prepregs employing an epoxy resin as a matrix resin. Although the prepreg may be prepared by impregnating the reinforcing woven fabric with the resin composition after the resin composition is dissolved in an appropriate solvent (i.e., wet process), if the above-described epoxy resin composition is used, a prepreg having no porosity can be prepared by the non-solvent method (hot-melt method) by which pores are otherwise likely to be formed. Since the above-described epoxy resin has high viscosity and yet has thixotropic property, the resin coating by the hot-melt method is unexpectedly easy.

When the solid rubber has a weakly cross-linked structure, it may form micro-phases dispersed in the epoxy resin so as to give high viscosity and high thixotropic property to the resin. If the prepreg employing this resin as a matrix resin is used as a surface material of the honeycomb fabricated panel, the formation of pores which likely to be formed in the interlayer zones is drastically reduced. Since the epoxy resin composition containing the solid rubber has high viscosity and yet has thixotropic property, the resin coating by the hot-melt method is unexpectedly easy.

Further, the addition of the solid rubber having the weakly cross-linked structure promotes the flexibility and adhesiveness of the resin, so that appropriate tackiness and drapability are given, while not deteriorating the high elastic modulus, high thermal resistance and high solvent resistance which are intrinsic to a thermosetting resin.

When a resin film is prepared by the hot-melt method, if the viscosity of the resin is high, film-formation is usually difficult. However, since the solid rubber having a weakly cross-linked structure gives high thixotropy even if the viscosity is high, the resin coating by the hot-melt method is unexpectedly easy.

In cases where the solid rubber having a weakly cross-linked structure is used, when a prepreg is produced

by the hot-melt method, the impregnation of the resin may preferably be carried out in two steps wherein the impregnation pressure in the first step is higher than in the second step. In this case, the resin composition which is impregnated in the first impregnation step may preferably have a complex coefficient of viscosity $\eta_{0.02}$ measured at 80°C under a vibration frequency of 0.02 Hz of not less than 5000 poise and less than 40,000 poise, and the resin composition which is impregnated in the second impregnation step may preferably have a complex coefficient of viscosity $\eta_{0.02}$ measured at 80°C under a vibration frequency of 0.02 Hz of 40,000 - 400,000 poise. Further, it is preferred to impregnate a resin composition containing an epoxy resin, at least one curing agent selected from the group consisting of aromatic amine curing agents, acid anhydride curing agents, dicyandiamide curing agents and novolak curing agents, and a solid rubber, in the first impregnation step and to impregnate a resin composition further containing polyether sulfone in addition to the components just mentioned above in the second impregnation step.

In the thus obtained prepreg, the resin composition impregnated in the first impregnation step constitutes an inner layer and the resin composition impregnated in the second impregnation step constitutes a surface layer. This structure is preferred since the porosity in the cured plate can be made small.

By dividing the impregnation process into two steps, the resin content of the prepreg after the first step may be made small so that the pressing out of the resin can be prevented even if a high impregnation pressure is applied. As a result, the quality of the finally obtained prepreg can be made high and the porosity of the fabricated plate can be extremely reduced.

In view of effectively preventing the pressing out of the resin even when a high impregnation pressure is applied and providing a prepreg having good impregnation property so as to provide a final prepreg having high quality, the resin content W_R of the intermediate prepreg after the first impregnation step may preferably be 25 - 30%, more preferably 27 - 29%. The resin content of the final prepreg may usually be 30 to 50%, although not restricted, irrespective whether the prepreg is prepared by the two-step process or one-step process.

The impregnation linear pressure (maximum contact stress) applied during the first impregnation step may preferably be not less than 1000 kg/cm², more preferably not less than 1200 kg/cm².

The impregnation linear pressure (maximum contact stress) σ_H (kg/cm²) is calculated from the following Hertz' elastic contact theory when two cylindrical rolls made of the same material are used:

$$\sigma_H(\text{kg/cm}^2) = 0.418(PE/Lr^*)^{1/2}$$

(wherein P represents the load applied to the rolls, E represents the elastic modulus of the rolls, L means the contact length of the rolls, r^* represents radius of curvature represented from radii r_1 and r_2 of the two rolls which is calculated from the following equation:

$$(1/r_1) + (1/r_2) = 1/r^*)$$

By preparing an intermediate prepreg having a good impregnation property in the first impregnation step, even if the second impregnation step is carried out at an impregnation pressure which is low enough to prevent the pressing out of the resin, a final prepreg having good impregnation property can be obtained. The thus obtained prepreg has a high stability of the resin content W_R, and its tackiness is also good.

In view of preventing the reduction in strength due to voids and preventing the degradation of the physical properties of the composite due to the repeated freezing of water, the ratio B of the area occupied by the voids in an optional cross-section may preferably be not more than 0.5%.

The impregnation property can be evaluated by curing the prepreg under the conditions in which the matrix resin does not substantially flow during the curing reaction, observing a polished cross-section of the cured prepreg and determining the percentage of the area of the non-impregnated region.

To clearly distinguish non-impregnated region from impregnated region when a cross-section of the prepreg is observed, it is necessary to polish the cross-section. To this end, it is necessary to heat the prepreg to cure. However, if a thermosetting matrix resin is heated, the viscosity is once decreased with the raise of the temperature and flowing of the resin is observed. If the resin flows during the curing process, the resin flows into the regions which are not impregnated in the original prepreg, so that the impregnation property thus determined does not reflect the state of the original prepreg. Therefore, in the curing of the prepreg, the increase in the viscosity due to the reaction of the resin must be more than the decrease in the viscosity due to the raise of the temperature. This may be attained by gradually raising the temperature to cure the resin. For example, in cases where a resin mixture containing a mixture of glycidylamine type epoxy resin and bisphenol A type epoxy resin; and an equivalent amount of diaminodiphenylsulfone as a curing agent is used, the preferred rate of raising temperature is not more than 1°C/hour.

When a polished cross-section of the thus cured prepreg is observed with an optical microscope, the non-impregnated regions in the prepreg is observed as voids in which the matrix resin does not exist. The void content B is calculated by the following equation:

$$B = (b/a) \times 100\ (\%)$$

(wherein "a" represents the area of an optional region in a photomicrograph of a cross-section and "b" represents the area occupied by voids).

The relationship between the void content B and the porosity P in the composite will now be described.

The methods for fabricating the composite using a prepreg include vacuum bag method, autoclave method using a vacuum bag and press method. Among these, to fabricate a composite with high performance, autoclave method using a vacuum bag is preferably employed.

Thus, a composite was prepared by the autoclave method using a vacuum bag, employing a prepreg whose void content B is known, and the optional region in an optional polished cross-section was observed with a microscope. As a result, a positive correlation was observed between the void content B and the porosity P in the composite. That is, if the void content B is small, the porosity P in the composite is small. Further, it was found that if the void content B is not more than 0.5%, by employing a prepreg which is appropriately flow-controlled, a composite having a porosity of substantially 0 can be obtained. Although the upper limit of the void content B of the more preferred range is 0.3%, it is not necessary to lower the void content B below the lower limit of 0.05%. If the void content B is unnecessarily low, in the wet method, a drying step at a high temperature for a long time is necessary to evaporate the solvent more, and in the hot-melt method, a higher temperature is necessary to decrease the viscosity of the resin, so that in both cases, the reaction of the resin is accelerated. As a result, the tackiness and drapability of the prepreg may be deteriorated.

The present invention will now be described by way of examples thereof. It should be noted that the examples are presented for the illustration purpose only and should not be interpreted in any restrictive way.

Example 1

An epoxy resin composition having the following composition was prepared in a kneader. The resin composition was heated at 80°C for a short time and coated on a releasing paper to obtain a resin film. In the following Examples and Comparative Examples, all parts are by weight unless otherwise specified.

<Epoxy Resin>	
Brominated bisphenol A type Solid Epoxy (EPC152)	13.4 parts
Bisphenol A type Liquid Epoxy (EP 828)	26.8 parts
Tetraglycidyldiaminodiphenyl methane (ELM 434)	17.0 parts
Bisphenol F type Liquid Epoxy (EPC830)	8.5 parts
<Curing Agent>	
4,4'-DDS (4,4'-diaminodiphenylsulfone)	23.0 parts
BF_3·MEA (BF_3 monoethylamine complex)	0.3 parts
<Solid Rubber>	
Carboxyl-terminated solid NBR having weakly cross-linked structure	8.0 parts
<Thermoplastic Resin>	
Hydroxyl-terminated polyether sulfone (PES100P)	3.0 parts
Total	100.0 parts

This resin film was set in a prepreg machine and impregnated into a plain-weaved fabric made of carbon fibers (TORECA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric, to obtain a prepreg having a resin content W_R of 40%. This prepreg had an excellent tackiness and drapability, and its cover factor K_p was 99%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken, which is shown in Fig. 1. In the entire cross-section, pores are not substantially observed and the porosity P was 0.05%.

Twenty of the thus prepared prepregs were laid-up in the same direction and the resulting laminate was cured. The toughness G_{IC} of the obtained cured plate was measured by the double cantilever method, which

was 9.5 pounds/inch.

Two prepregs were laid-up and the laminate was cured. The resulting cured plate was tested for its burn-through characteristics. The cured plate was placed on a tripod and heated with a gas burner under the cured plate. The time required for the flame to penetrate the plate was measured, which was 280 seconds.

Comparative Example 1

An epoxy resin composition having the following composition was prepared in a kneader. The resin composition was heated at 80°C for a short time and coated on a releasing paper to obtain a resin film.

```
<Epoxy Resin>


Brominated bisphenol A type Solid Epoxy      13.4 parts
(EPC152)

Bisphenol A type Liquid Epoxy (YD 128)       26.8 parts

Tetraglycidyldiaminodiphenyl methane         17.0 parts
(ELM 434)

Bisphenol F type Liquid Epoxy (EPC830)        8.5 parts

<Curing Agent>

4,4'-DDS (4,4'-diaminodiphenylsulfone)       23.0 parts

BF3·MEA (BF3 monoethylamine                   0.3 parts
complex)

<Liquid Rubber>

Epoxy-terminated liquid NBR (TSR-601)         8.0 parts

<Thermoplastic Resin>

Hydroxyl-terminated polyether sulfone         3.0 parts
(PES100P)

                                 Total      100.0 parts
```

This resin film was set in a prepreg machine and impregnated into a plain-weaved fabric made of carbon fibers (TORECA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric, to obtain a prepreg having a resin content W_R of 40%. The cover factor K_p of this prepreg was 92%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken, which is shown in Fig. 2. Pores are observed in the substantial area of the interlayer zones and the porosity P was 3.0%.

Twenty of the thus prepared prepregs were laid-up in the same direction and the resulting laminate was cured. The toughness G_{Ic} of the obtained cured plate was measured by the double cantilever method, which was 3.5 pounds/inch.

Two of the prepreg were laid-up and the laminate was cured. The resulting cured plate was tested for its burn-through characteristics. The cured plate was placed on a tripod and heated with a gas burner under the cured plate. The time required for the flame to penetrate the plate was measured, which was 130 seconds.

Example 2

An epoxy resin composition having the following composition was prepared in a kneader. The resin composition was heated at 80°C for a short time and coated on a releasing paper to obtain a resin film. The weight of the resin paper was 40 g/m².

Epoxy Resin Composition for First Step Impregnation

<Epoxy Resin>

Brominated bisphenol A type Solid Epoxy (EPC152)	13.7 parts
Bisphenol A type Liquid Epoxy (YD 128)	20.3 parts
Tetraglycidyldiaminodiphenyl methane (ELM 434)	17.3 parts
Bisphenol F type Liquid Epoxy (EPC830)	16.7 parts

<Curing Agent>

4,4'-DDS (4,4'-diaminodiphenylsulfone)	23.5 parts
BF_3·MEA (BF_3 monoethylamine complex)	0.5 parts

<Liquid Rubber>

Epoxy-terminated liquid NBR (TSR-601)	7.0 parts

<Thermoplastic Resin>

Hydroxyl-terminated polyether sulfone (PES100P)	1.0 part
Total	100.0 parts

This resin film was set in a prepreg machine and the first impregnation step was carried out by impregnating the resin composition into a plain-weaved fabric made of carbon fibers (TORECA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric. The impregnation temperature was 130°C and the impregnation linear pressure was 1400 kg/cm². The resin content W_R of the intermediate prepreg obtained in this first impregnation step was 29%. In spite of the high impregnation pressure, the resin was not pressed out and an intermediate prepreg having the prescribed resin content was obtained.

A resin composition for the second impregnation step, which had the same composition as that for the first impregnation step was coated on a releasing paper to obtain a resin film having a weight of 25 g/m². The second impregnation step was carried out by impregnating the intermediate prepreg obtained in the first impregnation step with the resin composition from both sides of the prepreg under heat. The impregnation temperature was 100°C and the impregnation linear pressure was 690 kg/cm². A prepreg having a resin content W_R of 40% was obtained. The thus obtained final prepreg had excellent impregnation property, tackiness and drapability. The cover factor K_p of the thus obtained final prepreg was 98%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken. Pores were not substantially observed in the interlayer zones and the porosity P was 0.04%.

Comparative Example 2

Using the epoxy resin composition used in Example 2, a prepreg was prepared by a single impregnation step.

That is, the epoxy resin composition was heated at 80°C for a short time and was coated on a releasing paper to obtain a resin film having a weight of 65 g/m². This resin film was set in a prepreg machine and impregnation was carried out in a single step by impregnating the resin composition into a plain-weaved fabric made of carbon fibers (TORECA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric. The impregnation temperature was 120°C and the impregnation linear pressure was 1400 kg/cm². When the resin composition was pressed to the reinforcing fabric under a high pressure, the resin was pressed out, so that the obtained prepreg had a resin content W_R of only 34%. The cover factor K_p of this prepreg was 95%.

Comparative Example 3

A prepreg was prepared by the same process as in Comparative Example 2 except that the impregnation linear pressure was 900 kg/cm². When the resin composition was pressed to the reinforcing fabric, the resin was not pressed out and a prepreg having a resin content W_R of 40% was obtained. The cover factor K_p of this prepreg was 98%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken. Pores were observed in substantial parts of the interlayer zones and a number of pores were observed in the resin layer, which are considered to be formed due to the insufficient impregnation of the resin. The porosity P was 1.5%.

Comparative Example 4

Using the resin composition used in Example 2, a prepreg was prepared by a two-step impregnation process. The resin composition formulated in a kneader was heated at 80°C for a short time and was coated on a releasing paper to obtain a resin film having a weight of 40 g/m². This resin film was set in a prepreg machine and a first impregnation step was carried out by impregnating the resin composition into a plain-weaved fabric made of carbon fibers (TORECA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric. The impregnation temperature was 130°C and the impregnation linear pressure was 690 kg/cm². The resin content W_R of the thus obtained intermediate prepreg obtained by this first impregnation step was 29%.

The epoxy resin composition having the same composition as that used in the first impregnation step was coated on a releasing paper to obtain a resin film for the second impregnation step, having a weight of 25 g/m². The intermediate prepreg obtained by the first impregnation step was impregnated with the epoxy resin composition to carry out the second impregnation step. The impregnation linear pressure was 690 kg/cm² which was the same as that in the first impregnation step, and the impregnation temperature was 100°C. A final prepreg having a resin content W_R of 40% was obtained. The cover factor K_p of this prepreg was 98%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken. Pores were observed in substantial parts of the interlayer zones and a number of pores were observed in the resin layer, which are considered to be formed due to the insufficient impregnation of the resin. The porosity P was 2.5%.

Reference Example 1

Using "TORECA" T300 filaments (average number of twisting: 0.8 turns/m, average diameter of single fiber: 7 μm, average number of fibers per filament: 3000, fineness: 1800 denier, specific gravity: 1.76) as warps and woofs, a woven fabric was prepared by plain weaving. The widths of each warp and woof were 1.47 mm and 1.49 mm, respectively, and the size of the meshes was 0.57 mm and 0.59 mm in the directions of warp and woof, respectively. The weaving densities in the warp and woof directions were both 4.85 filaments/cm (warp pitch: about 2.06 mm). The weight of the fabric was 194 g/cm² and the thickness of the fabric was 0.31mm.

The above-described woven fabric was made to run in the warp direction at a rate of 1.5 m/min and the opening, width-enlarging and flattening operation of the filaments was performed by using water jets. The diameter of the nozzle was 0.13 mm, the nozzle pitch was 0.6 mm and the beating force per one water jet was 0.6 gf.

In the thus treated woven fabric, the filaments were well opened and the widths of the warps and woofs were enlarged to 1.71 mm and 1.91 mm, respectively. The thickness was 0.28 mm, and the cover factor K_c was 99%. The obtained woven fabric was thin and the irregularities in the surface were very small. Further, cutting of single fibers and generation of down were not observed.

Example 3

An epoxy resin composition having the following composition was prepared in a kneader.

```
<Epoxy Resin>

Brominated bisphenol A type Solid Epoxy          63.0 parts
(EPC152)

Bisphenol A type Liquid Epoxy (EPC828)          127.0 parts

Tetraglycidyldiaminodiphenyl methane             40.0 parts
(ELM 434)



Bisphenol F type Liquid Epoxy (EPC830)           20.0 parts

<Curing Agent>

4,4'-DDS (4,4'-diaminodiphenylsulfone)           80.0 parts

<Solid Rubber>

Carboxyl-terminated solid NBR (NIPOL 1072)       25.0 parts
                                                 (7.0 wt%)
```

During the process of heating this resin composition from 50°C at a rate of 1.5°C/min, the complex coefficient of viscosity $\eta_{0.5}$ measured at 80°C under a vibration frequency of 0.5 Hz was 700 poise and the minimum complex coefficient of viscosity η_{min} was 90 poise.

This resin composition was heated at 80°C for a short time and was coated on a releasing paper to obtain a resin film.

This resin film was set in a prepreg machine and impregnation of the resin was performed from the both sides of the carbon fiber woven fabric prepared in Reference Example 1. The impregnation temperature was 100°C and the impregnation pressure was 4 kgf/cm² to obtain a prepreg with a resin content of 40%, having excellent tackiness and drapability were obtained. The cover factor K_p of this prepreg was 99%. This prepreg was cured in a hot air oven by heating the prepreg to 180°C at a rate of 0.5 °C/hour. A photomicrograph of a polished cross-section of the cured prepreg was taken and the void content B was measured, which was 0.15%.

One prepreg thus obtained was placed on an aluminum plate to which a silicone-based releasing agent was applied. On the prepreg, another prepreg was placed such that the direction of warps of the reinforcing fabric of the prepreg was shifted by 45° from the direction of warps of the reinforcing fabric of the first placed prepreg. On the second prepreg, a honeycomb core made of aramide paper impregnated with a thermally resistant phenol resin, having a size of the inner space of the cells of 1/8 inch (about 3.2 mm) and having a thickness of 1/2 inch (about 12.7 mm) was placed. On the honeycomb core, the above-described two prepregs were laminated in the direction such that their reinforcing fabrics constitute the mirror image of the reinforcing fabrics of the above-mentioned first two prepregs under the honeycomb core. The entire structure was packed in a fluorine-contained resin film.

The resulting packed structure was placed in an autoclave and was heated to 180°C at a rate of 1.5°C/min under a pressure of 3 kgf/cm² while reducing the pressure in the pack. The structure was left to stand at this temperature for two hours to cure the epoxy resin of the cloth prepreg to form skins and to adhere the skins with the honeycomb core.

A cross-section of the thus obtained honeycomb sandwich panel was observed with a microscope, which is shown in Fig. 3. The porosity P was 0.01%.

Comparative Example 5

The same procedure as in Example 3 was repeated except that carbon fiber woven fabric "C07373Z" of which filaments are not opened was used as the reinforcing fabric. The cover factor K_p was 96%. The porosity P of the obtained composite was 0.3%, which is inferior to that attained in Example 3.

Comparative Example 6 (Less Preferred)

The same procedure as in Example 3 was repeated except that 12% by weight of a solid NBR "NIPOL 1072" was used. The cover factor K_p of the obtained prepreg was 99%. Although the minimum complex coefficient of viscosity η_{min} was raised to 500 poise, the complex coefficient of viscosity $\eta_{0.5}$ at 80°C was 2500 poise, so that the void content B was as much as 0.8%. As a result, the porosity P of the obtained composite was 0.5%, which was inferior to that attained in Example 3.

Comparative Example 7 (Less Preferred)

The same procedure as in Example 3 was repeated except that 3% by weight of a solid NBR "NIPOL 1072" was used. The cover factor K_p of the obtained prepreg was 99%. Since the complex coefficient of viscosity $\eta_{0.5}$ at 80°C was as low as 350 poise, the void content B was as much as 0.8%. The minimum complex coefficient of viscosity was as low as 15 poise, so that the porosity P of the composite was 0.4%, which was inferior to that attained in Example 3. A photomicrograph of a cross-section of the honeycomb sandwich panel is shown in Fig. 4.

The results of Example 3 and Comparative Examples 5 - 7 are shown in Table 1.

Table 1

	Example 3	Comparative Example 5	Comparative Example 6	Comparative Example 7
Type of Carbon Fiber Fabric	Opened	Non-opened	Opened	Opened
Amount of "NIPOL 1072" Added(%)	7	7	12	3
Viscosity at 80 °C (poise)	700	700	2500	350
Minimum Viscosity (poise)	90	90	500	15
Void Content B(%) in Prepreg	0.15	0.6	0.8	0.1
Porosity P(%) of Composite	0.01	0.3	0.5	0.4

Claims

1.   A cloth prepreg comprising a resin composition including an epoxy resin, a curing agent and a solid rubber, and a woven fabric made of reinforcing fibers, the meshes of said woven fabric being crushed such that said prepreg has a cover factor K_p of 97 - 99,9%.

2. The cloth prepreg of claim 1, wherein said solid rubber is solid acrylonitrile-butadiene rubber.

3. The cloth prepreg of claim 2, wherein said solid rubber is a solid acrylonitrile-butadiene rubber having a functional group.

4. The cloth prepreg of claim 3, wherein said functional group is carboxylic group.

5. The cloth prepreg of any preceding claim, wherein said solid rubber is a solid acrylonitrile-butadiene rubber having a weakly cross-linked structure.

6. The cloth prepreg of any preceding claim, wherein said resin composition has a complex coefficient of viscosity $\eta_{0.02}$ determined at 80°C under a vibration frequency of 0.02 Hz of not less than 5000 poise, and a complex coefficient of viscosity η_2 determined at 80°C under a vibration frequency of 2 Hz and said complex coefficient of viscosity $\eta_{0.02}$ satisfy the equation of:

    $$\log\eta_{0.02} - \log\eta_2 \geqq 0.5.$$

7. The cloth prepreg of any preceding claim, wherein said resin composition further comprises polyether sulfone.

8. The cloth prepreg of any preceding claim, wherein said curing agent is at least one selected from the group consisting of aromatic amine curing agents, acid anhydride curing agents, dicyandiamide curing agents and novolak curing agents.

9. The cloth prepreg of any preceding claim, wherein said solid rubber at least partially forms three-dimensional network and dispersed so as to attain micro-phase separation in non-cured resin composition.

10. The cloth prepreg of any preceding claim, wherein said resin composition has a complex coefficient of viscosity $\eta_{0.5}$ determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 100 - 1500 poise, and has a minimum complex coefficient of viscosity η_{min} determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 50 - 300 poise.

11. The cloth prepreg of any preceding claim, wherein said woven fabric has warps and woofs made of multifilament carbon fibers, the widths W (mm) and finenesses D (denier) of said warp and woof satisfying the equation of:

    $$W = k \cdot (D/\rho)^{5/9}$$

    (wherein k represents 3.5 x 10^{-2} - 10.0 x 10^{-2} (mm·D$^{-5/9}$) and ρ represents specific gravity of said carbon fibers),
    and wherein said woven fabric has a cover factors K_c of 90.0 - 99.8%.

12. The cloth prepreg of any preceding claim, comprising two kinds of resin compositions having different coefficients of viscosity, which constitute inner layer and surface layer, respectively, the resin composition constituting said surface layer having a complex coefficient of viscosity $\eta_{0.02}$ determined at 80°C under a vibration frequency of 0.02 Hz of 40,000 - 400,000 poise, the resin composition constituting said inner layer having a complex coefficient of viscosity $\eta_{0.02}$ determined at 80°C under a vibration frequency of 0.02 Hz of not less than 5000 poise and less than 40,000 poise.

13. The cloth prepreg of claim 12, wherein both of said two kinds of resin compositions comprise an epoxy resin, a curing agent selected from the group consisting of aromatic amine curing agents, acid anhydride curing agents, dicyandiamide curing agents and novolak curing agents, and a solid rubber, the resin constituting said surface layer further comprising polyether sulfone.

14. The cloth prepreg of any preceding claim, wherein the area occupied by voids in an optional cross-section is not more than 0.5%.

15. A process of producing the cloth prepreg of claim 1, comprising impregnating a resin composition containing said epoxy resin, said curing agent and a solid acrylonitrile-butadiene rubber having a functional group and having a weakly cross-linked structure into said woven fabric in two steps, wherein in the first impregnation step, the resin composition is impregnated so as to attain resin content W_R of 10 - 30%.

16. The process of claim 15, wherein the pressure applied in said first impregnation step is higher than that in the second impregnation step, and the maximum impregnation linear pressure in said first impregnation step is not less than 1000 kg/cm².

17. The process of claim 15 or 16, wherein the resin composition impregnated in the first impregnation step has a complex coefficient of viscosity $\eta_{0.02}$ determined at 80°C under a vibration frequency of 0.02 Hz of not less than 5000 poise and less than 40,000 poise, and the resin composition impregnated in said second impregnation step has a complex coefficient of viscosity $\eta_{0.02}$ determined at 80°C under a vibration frequency of 0.02 Hz of 40,000 - 400,000 poise.

18. The process of claim 15, 16 or 17, wherein the pressure applied in said first impregnation step is higher than that in the second impregnation step.

19. A process of producing the cloth prepreg of claim 1, comprising the step of impregnating a resin composition containing said epoxy resin, said curing agent and a solid acrylonitrile-butadiene rubber having a functional group and not having a weakly cross-linked structure into a woven fabric having warp and woof made of multifilament carbon fibers, the widths W (mm) and finenesses D (denier) of said warp and woof satisfying the equation:

$$W = k \cdot (D/\rho)^{5/9}$$

wherein k represents $3.5 \times 10^{-2} - 10.0 \times 10^{-2}$ (mm·D$^{-5/9}$) and ρ represents specific gravity of said carbon fibers ,
said woven fabric having a cover factor K_c of 90.0 - 99.8%.

20. The process of claim 19, wherein said resin composition has a complex coefficient of viscosity $\eta_{0.5}$ determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 100 - 1500 poise, and has a minimum complex coefficient of viscosity η_{min} determined at 80°C under a vibration frequency of 0.5 Hz during heating from 50°C at a rate of 1.5°C/min of 50 - 300 poise.
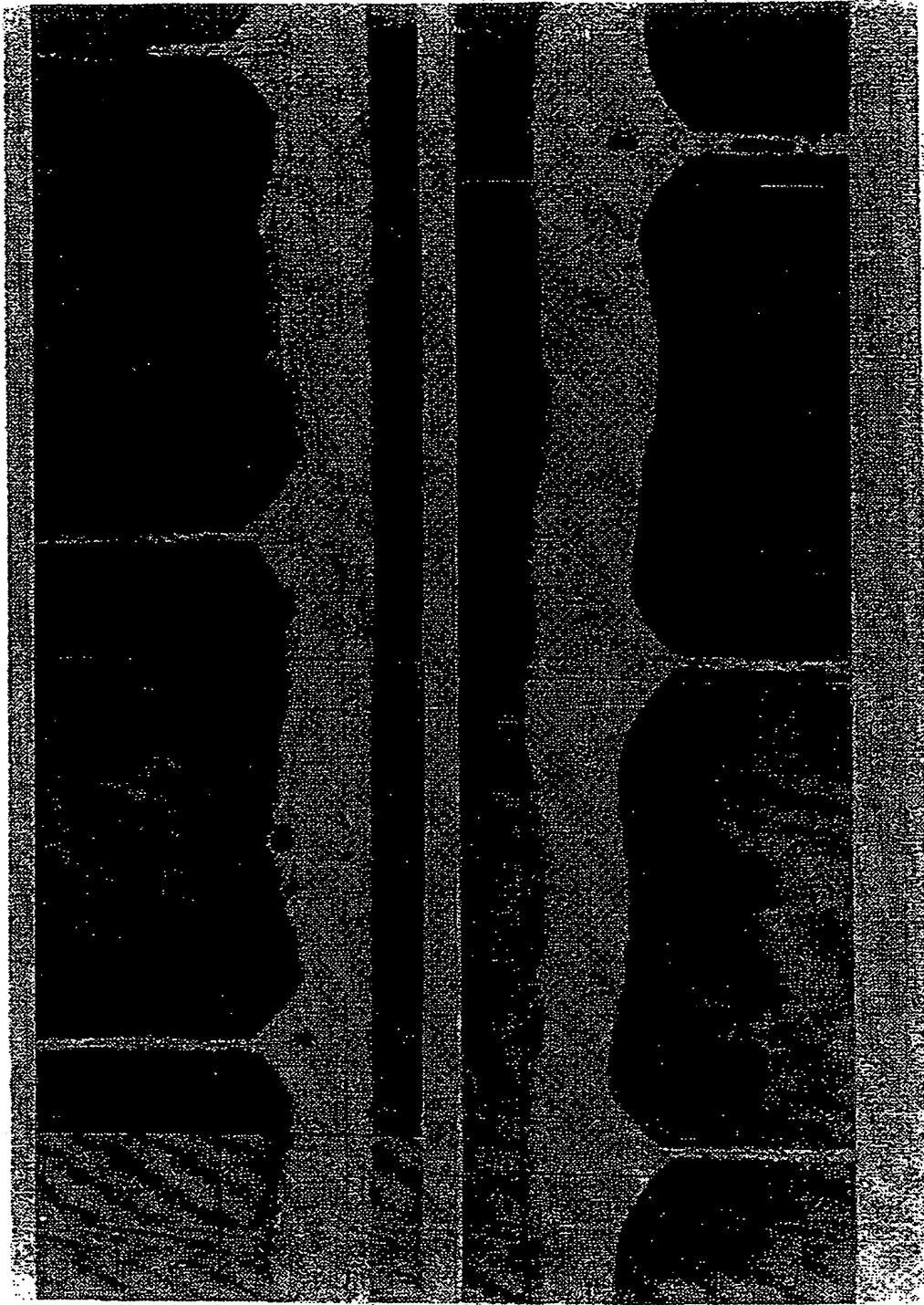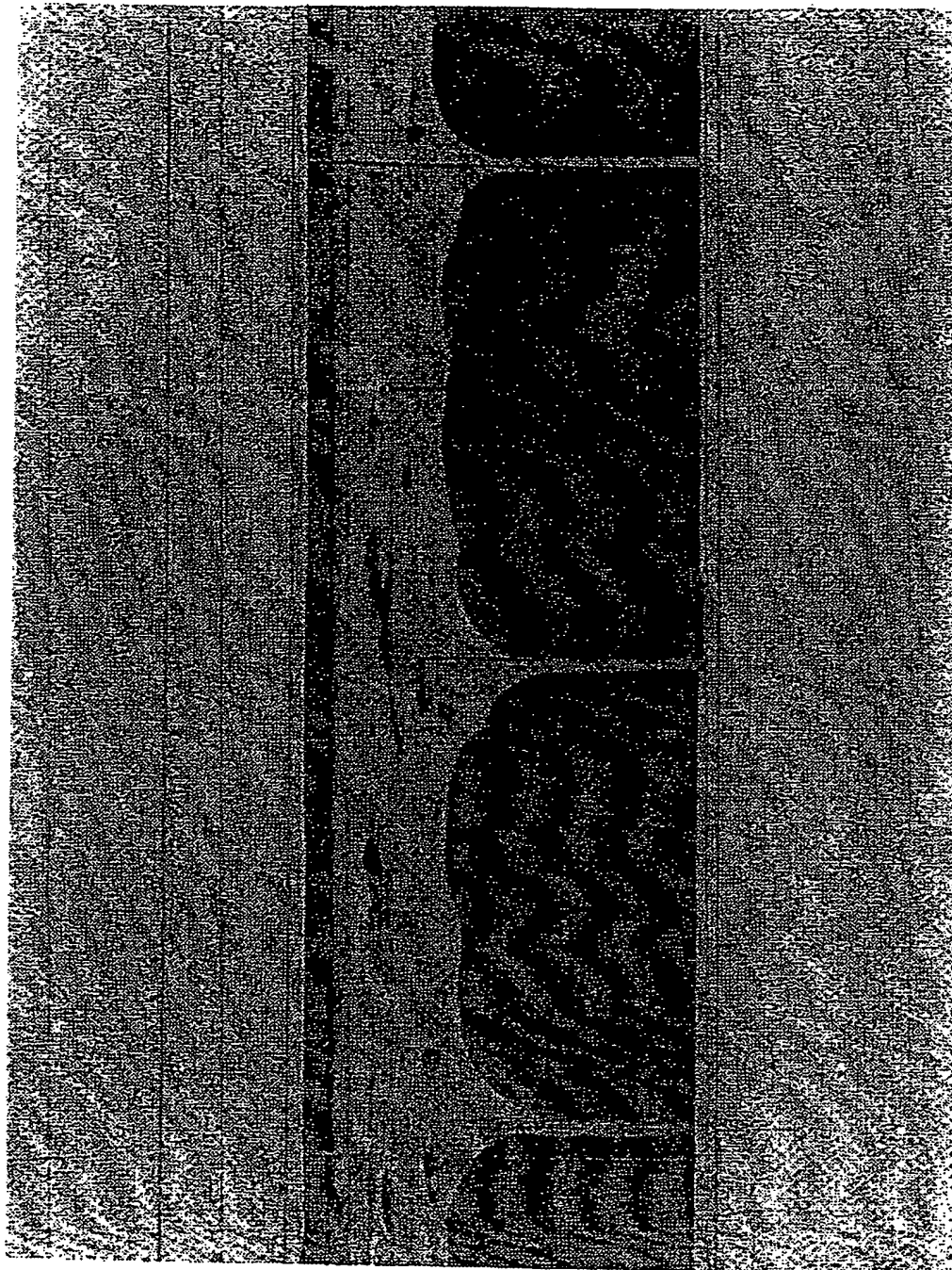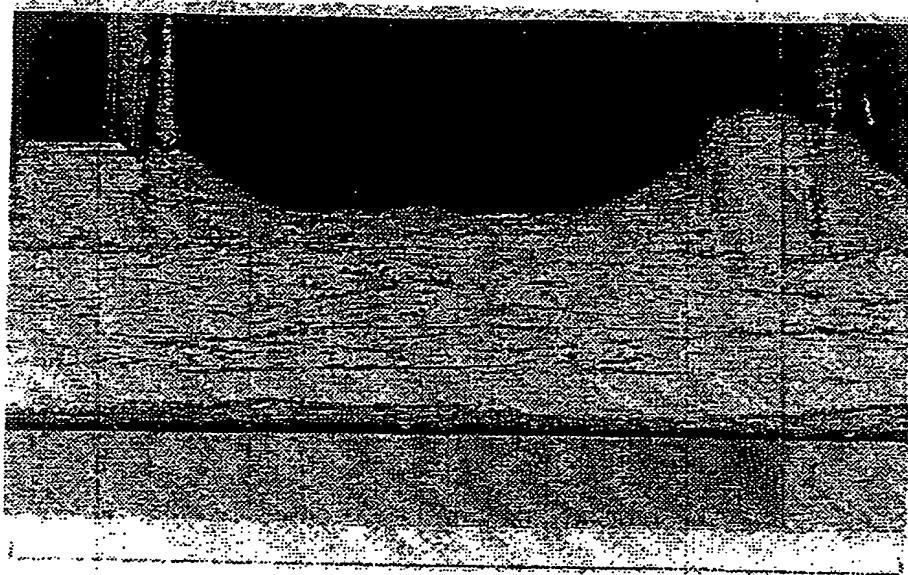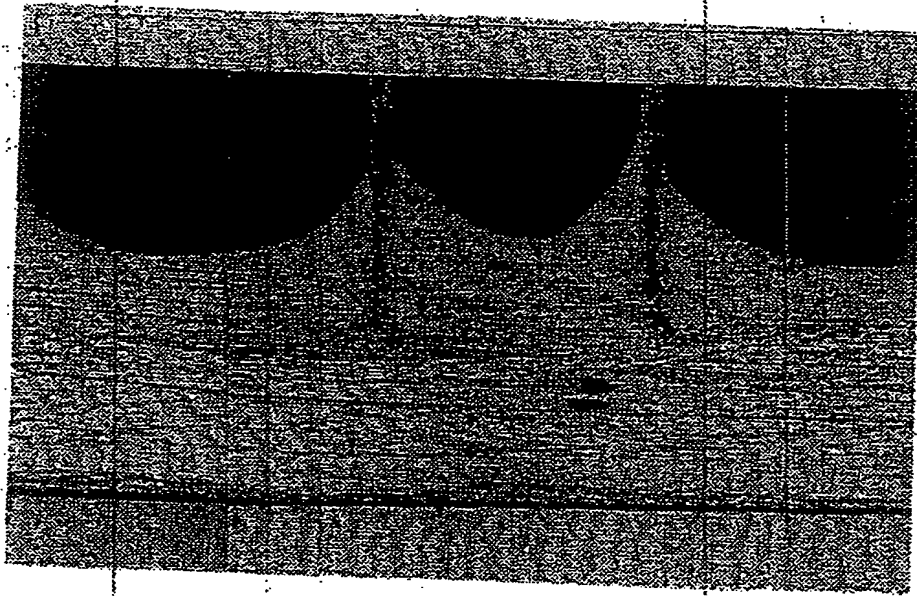
Fig. 1

Fig. 2

Fig. 3

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number

EP 93 30 1587

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DE-A-2 825 191 (KOBAYASHI, TUGUO) * claim 1 * * figures 1,2 * * page 13, line 8 - page 15, line 1 * ---	1-5,9,10	C08J5/24 B29C67/14
Y	EP-A-0 351 028 (AMOCO CORPORATION) * claims 1,3,4,9 * * page 4, line 10 - line 18 * * page 4, line 32 - line 37 * * page 5, line 9 - line 10 * * page 6, line 21 - line 28 * * page 8, line 1 - line 7 * ---	1-5,9,10	
A	EP-A-0 434 013 (MITSUBISHI PETROCHEMICAL CO., LTD.) * claims 1,3 * ---	1-4,8	
A	EP-A-0 262 891 (TOHO RAYON CO., LTD.) * claims 1,2,5,9,14,17,19 * * page 7, line 13 - line 22 * ---	1,2,7	
A	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 90-258317[34] & JP-A-2 182 409 (MATSUSHITA ELC. WORKS) 17 July 1990 * abstract * -----	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C08J B29D B29C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 JUNE 1993	NIAOUNAKIS M.

CATEGORY OF CITED DOCUMENTS

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